LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Low Temperature Phase Instability of the Gamma Phase in SnIn Alloys

S. Chu, C. Yanar, A. J. Schwartz, T. B. Massalski, D. E. Laughlin

August 22, 2005

Disclaimer

LOW TEMPERATURE PHASE INSTABILITY OF THE GAMMA PHASE IN SnIn ALLOYS

Shaoyan Chu[1]; Cagatay Yanar[2]; Adam J. Schwartz[3]; Thaddeus B. Massalski[1] and David E. Laughlin[1];

[1] Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213
[2] Alcoa Technical Center, Alcoa Center, PA 15069, USA
[3] Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore, California 94550, USA.

Abstract

The Sn-rich side of the Sn-In phase diagram has been investigated at temperatures ranging from 77 to 500 K by using X-ray diffraction, thermal analysis, and magnetization measurements. It is confirmed that the β-Sn(In) phase can remain as a metastable phase down to 77 K within the composition range of 86.3-94 at% of Sn. An isothermal displacive (martensitic) transition of the γ phase to the metastable β phase is suggested as the mechanism of the transformation.

1. Introduction

A significant part of scientific understanding of materials is based on the elucidation of how and why materials change under varying environmental conditions. We began our investigations of In-Sn alloys in view of our use of the third law of thermodynamics [1] to aid in the prediction of low temperature phase equilibria. Our premise is that phases in equilibrium at 0 K should have zero configurational entropy at zero K. This means that one should question the validity of a phase diagram if it displays an intermediate solid solution phase that appears to go to 0 K as the equilibrium phase. The third law would suggest that it should decompose into phases consisting of its elemental constituents or a combination of these with an atomically ordered phase. We started to think along these lines after reading S.S. Hecker review, which included two proposed phase diagrams for the technically important Pu-Ga system [2]. In one, the solid solution δ phase was thought to be stable to very low temperatures, while in the other, it was shown to decompose into two other phases. The In-Sn binary phase diagram was chosen for this investigation because of its γ phase[3].   See Figure 1. The γ intermediate phase can be seen to have a wide solubility and according to the diagram this phase field remains in existence to very low temperatures. Because of the low melting temperatures of the phase in this alloy system, diffusion at low temperatures may be possible. We address the application of the third law in a later paper.

There are two intermediate phases at room temperature and pressure, namely the β alloy and the γ alloy. This phase diagram is bounded at the In end by the In(Sn) tetragonal phase and on the Sn end by the terminal solid solution based on white tin, β-Sn(In) phase, above about 286 K and by
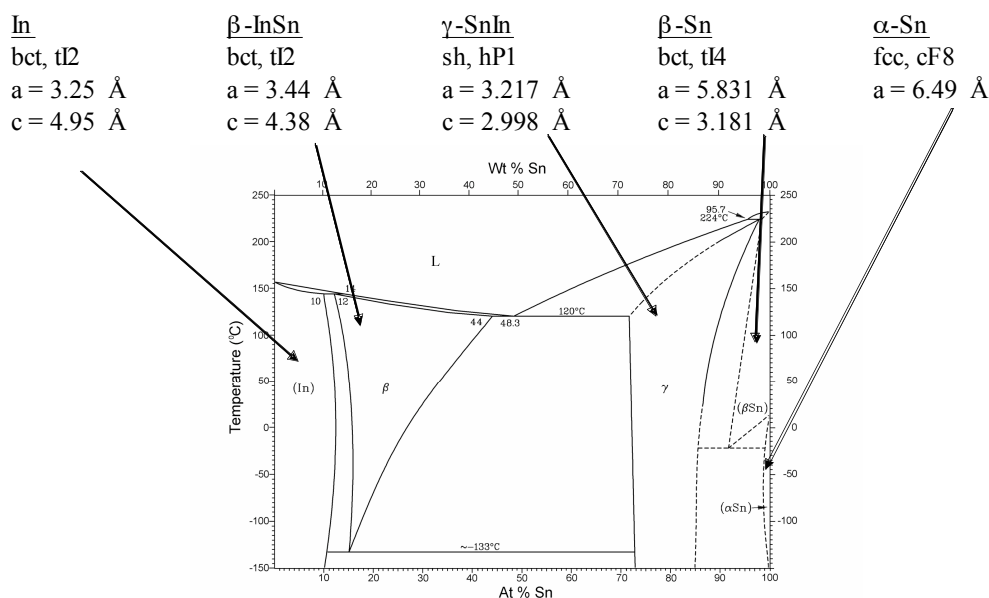
In	β-InSn	γ-SnIn	β-Sn	α-Sn
bct, tI2	bct, tI2	sh, hP1	bct, tI4	fcc, cF8
a = 3.25 Å	a = 3.44 Å	a = 3.217 Å	a = 5.831 Å	a = 6.49 Å
c = 4.95 Å	c = 4.38 Å	c = 2.998 Å	c = 3.181 Å	

Figure 1. Current accepted phase diagram of Sn-In.

gray tin, α-Sn phase, below. The phase transition from β-Sn(In) phase to α-Sn(In) phase is very slow, especially when the indium composition of the alloy in the solid solution reaches about 1 at%. X-ray diffraction revealed that an indium-rich intermediate β - InSn phase also with the bct structure decomposes to the bct phase of In(Sn) and Sn rich intermediate γ phase with simple hexagonal (sh) structure below about 140 K [4]. In this work we set out to see if the γ phase also decomposes at low temperatures, in line with our thinking about the third law of thermodynamics.

2. Experimental procedure

Alloys for this study were prepared from 99.999% pure tin and 99.9995% pure indium. Starting materials were melted in sealed silica tubes that were evacuated and flushed with argon. After holding the molten alloys for one hour, the silica tubes were quenched in ice water to minimize coring effects. As-cast ingots were then homogenized at 125°C for about a week. These ingots were cut and polished to form penny-like shapes, 7 mm in diameter and 0.7 mm high. These were annealed in evacuated silica tubes at 125°C for about 10 days and cooled to room temperature in the furnace. Except when mentioned, all of samples used in this work had an aging period at room temperature (~293 K) for more than three months before we performed measurements. The compositions of fourteen alloys Sn_xIn_{1-x} used in this study, where x=0.80, 0.81, 0.82, 0.83 0.84, 0.85, 0.86, 0.87, 0.88, 0.90, 0.91, 0.92, 0.94, and 0.96.

X-ray diffraction studies at low temperature were performed using a home-made cold-stage X-ray unit. The samples were mounted on the copper tip of this stage with a liquid nitrogen (LN_2) container. For performing the X-ray diffraction, samples treated at low temperature were transferred directly from a cool-bath container filled with LN_2 to the cold-stage without leaving the cryogen. A hot-stage X-ray holder was used for X-ray patterns at temperature from 293 K to
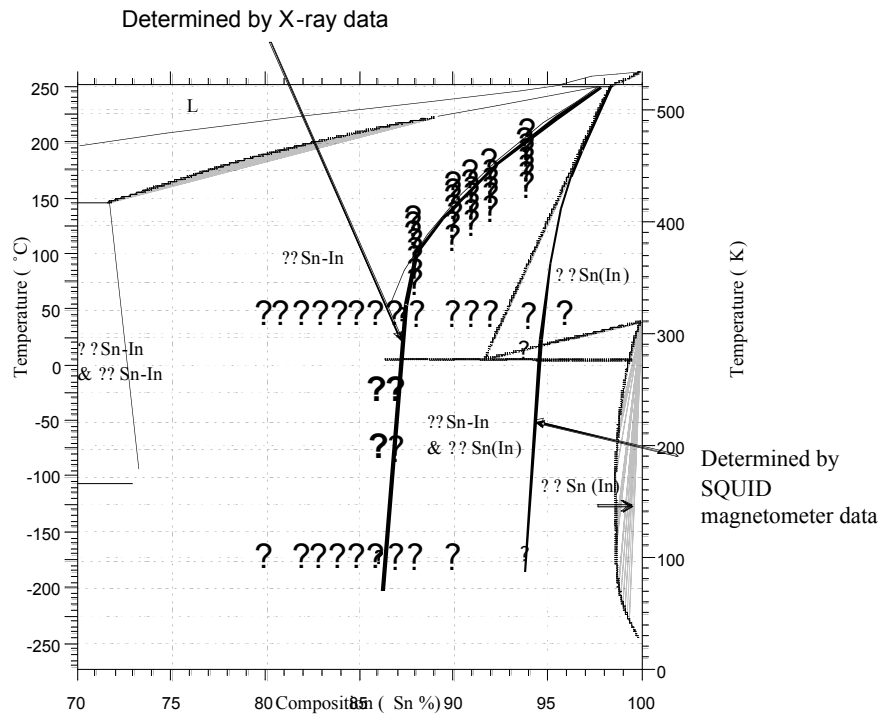
Figure 2. Phase diagram of tin-rich side of Sn-In system extended to low temperature. Phase boundaries of β, β+γ and γ regions are plotted with bold solid line. At very low temperature, a set of assumable boundaries is drawn in bold dashed lines.

450 K in air. X-ray diffraction studies were performed using Cu-K$_\alpha$ radiation using a Rigaku-GeigerFlex X-Ray machine. Lattice parameters were determined by using the Philips X'Pert Plus software for all the peaks between $2\theta = 20$ and 80 degree. CaRlne Crystallography 3.1 software was used for building up proposed lattice structures. Differential Scanning Calorimetry (DSC) analysis was performed to verify the melting and solidification temperatures of the alloys. Superconductivity of the terminal Sn-rich phase at low temperature was detected by a magnetometer with Superconducting Quantum Interference Devices (SQUID).

3. Results and discussions

3.1 Phase diagram

Figure 2 presents the results of our investigations on the Sn-In diagram within the concentration range of tin from 80 to 96 at% Sn and temperature from 77 to 500 K. Our liquidus measurements are in full agreement with the currently accepted experimental data, so we have not plotted them on this diagram.

At room temperature, samples containing between 87 and 94 at % Sn are in two-phase equilibrium. They can be reversibly transformed to the single γ-Sn-In phase at elevated temperatures which depend on their composition. The experimental points from X-ray structural studies in this work are shown in this diagram as circles. These data were obtained from X-ray diffraction patterns of samples before and after low temperature treatment. For the low temperature treatments, the samples were quenched to the designated temperature from room temperature within two seconds. For the samples which were held 14-days in LN$_2$ there was no

change in the X-ray diffraction patterns from alloys with concentration range of Sn from 80 to 86 at % except for a shift of peak's position caused by change of the lattice parameters due to thermal contraction. Holding for long times in LN_2 did not change this observation. For example, a sample of $Sn_{0.86}In_{0.14}$ shows the single γ-SnIn phase even though it was immersed in LN_2 for 156 days. However, a very weak peak of (211) from β-Sn(In) was observed at 94 K in a sample of $Sn_{0.87}In_{0.13}$ immersed in LN_2 for 14 days. This sample was single phase γ-SnIn at room temperature. As shown in Figure 3, when heated up from LN_2, the β-Sn(In) disappears at about 220 K. Thus, the β phase which forms at LN_2 temperature does so in an isothermal manner.

We also performed measurements on a SQUID magnetometer and found that at LN_2 temperatures, the 6% In alloy was single-phase β. This was determined by measuring the superconducting transition temperature of the sample and comparing it to the known values of β and γ. The principles and experimental details of these investigations will be published later. The two-phase field determined in this investigation is delineated in bold lines in Figure 2.

3.2 Low Temperature phase Transformation

Figure 4 shows the changes of X-ray patterns of a $Sn_{90}In_{10}$ sample under different heat treatments. The sample was held at room temperature for three months. After equilibrium was attained, the sample was quenched to 77 K and held in liquid nitrogen for fourteen days. The first θ-2θ X-ray scan for this sample was performed at 94 K. The sample was then warmed up to room temperature within about 40 minutes. The X-ray pattern was taken (labeled warm up to RT). Then the sample was quenched in liquid nitrogen again and performed a third θ-2θ scan at 94 K without delay.
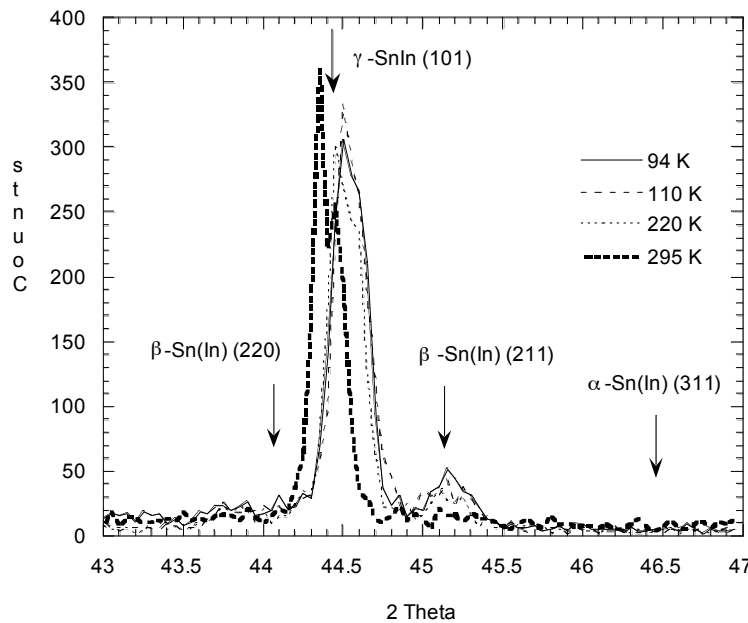

Figure 3. Temperature dependence of diffraction intensity for sample of $Sn_{0.87}In_{0.13}$. Before this measurement, the sample was quenched to 77 K from room temperature and immersed in LN_2 for 14 days.
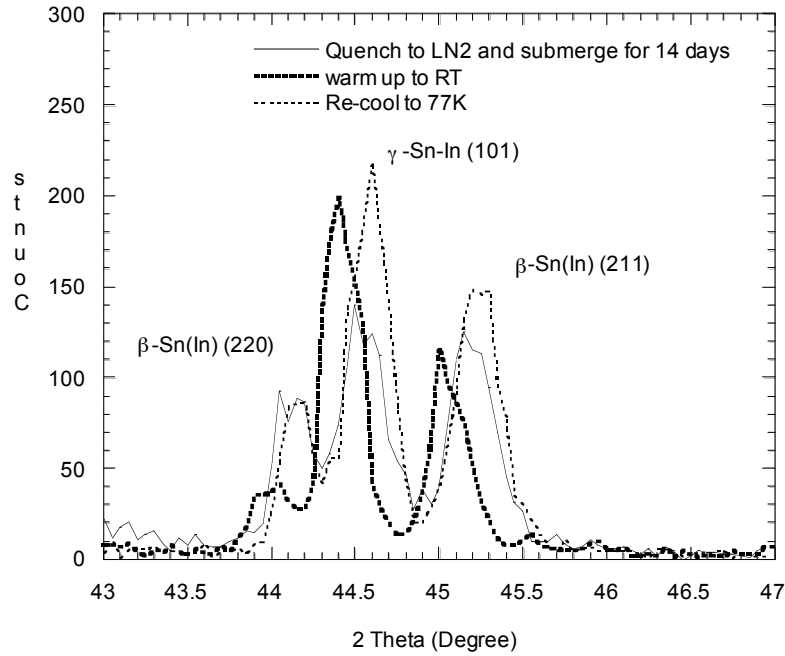
Figure 4. X-ray patterns of a $Sn_{90}In_{10}$ sample under different designed heat treatments.

The ratios of diffraction intensity from the two phases indicated that after the first treatment, i.e., quenched to 77 K and submerged in liquid nitrogen for fourteen days, the sample shows largest concentration of the β phase compared to the same sample warmed up to room temperature and that of re-quenched to liquid nitrogen without a long aging-time. The concentration of β phase in re-quenched sample is just a little higher than that of warmed up sample but much less than that of the sample held at 77 K for fourteen days. This demonstrates that there was a time dependent transformation (isothermal) at 77 K for the formation of the β phase. Other work was performed on samples quenched from high temperature and the transformation was observed to occur via an athermal martensitic transformation. Work on this is ongoing.

One half century ago, G. V. Raynor and J. A. Lee [5] proposed a description of the phase transition from γ-SnIn to β-Sn(In) as a shift in lattice stacking. According to this model, this simple hexagonal structure (*sh*) of the γ phase was expressed in terms of an orthorhombic unit cell which is redrawn in Figure 5. This shows that the axes of the γ phase can be indicated either $a_1 = a_2$ and c for simple hexagonal structure or a_γ, b_γ and c_γ for orthorhombic structure. If half of atoms in γ phase shuffle relative to the others in the direction of a_2 (or c_γ) by an amount equal to $a_2/4$ (or $c_\gamma/4$) and if each of the lattice parameters change, a structural transformation will occur. The lattice parameters of the β phase, indicated by a_β, b_β and c_β, are close to those of a_γ, b_γ and c_γ respectively. This model could be classified as a diffusionless/displacive or martensitic transformation (MT) [5,7].

4. Summary

The phase diagram of Sn-rich side of Sn-In system has been extended to low temperatures (~77 K). Structural analysis indicates that the β-Sn(In) phase is the metastable phase until 77 K

within the composition of 86.3-94 at% of tin. In general, the phase transition from the γ phase to the β phase is an isothermal displacive transformation (martensitic) depending on the exact starting conditions of the alloy.
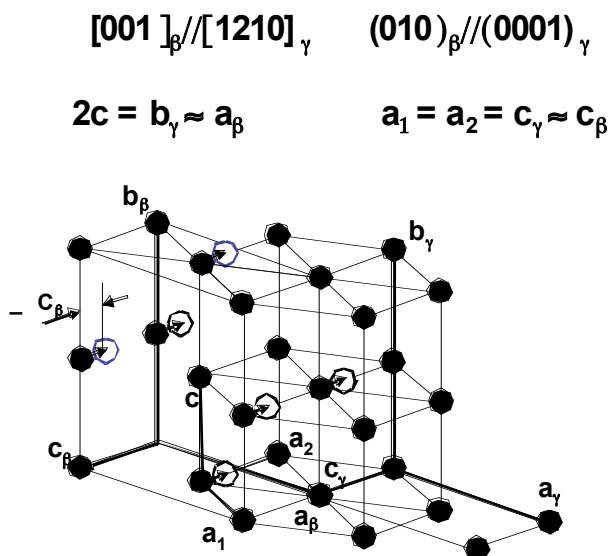
$$[001]_\beta // [1\overline{2}10]_\gamma \qquad (010)_\beta // (0001)_\gamma$$

$$2c = b_\gamma \approx a_\beta \qquad a_1 = a_2 = c_\gamma \approx c_\beta$$

Figure 5. Orthorhombic unit cell derived from simple hexagonal structure and structure relationships between the γ phase and the β phase.

References
1. J.P. Abriata and D.E. Laughlin, Progress in Materials Science 49, 367-387, 2004
2. Siegfried S. Hecker and Lidia F. Timofeeva, Los Alamos Science, Number 26, 224-251 (2000).
3. T.B. Massalski, H. Okamoto and L. Kacprzak, Binary Alloy Phase Diagrams, second edition, American Society for Metals, 1990.
4. S. F. Bartram, W. G. Moffatt and B. W. Roberts, J. Less-Com-mon Met., **62**(1-2), 11-27 (1978).
5. G. V. Raynor and J. A. Lee, ACTA Metallurgica, Vol. 2, July (1954).
6. Bain E. C. Trans AIME., **70**, 25 (1924).
7. K. Otsuka, X. Ren, T. Takeda, Scripta Materialia **45** 145-152 (2001).